



Ottawa Hull K1A 0C9

(21)	(A1)	2,130,767
(22)		1994/08/24
(43)		1996/02/25

(51) Int.Cl. <sup>5</sup> B01D-053/34; B01D-053/14

(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) SOx/NOx/Hg Removal from Flue Gas by Ammonia Wet Scrubbing Using Iron Chelate Catalysts

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(57) 16 Claims

Notice: This application is as filed and may therefore contain an incomplete specification.



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**ABSTRACT OF THE DISCLOSURE**

A method of removing contaminants from a flue gas provides the flue gas to an absorber tank. A metal chelate catalyst is  
5 provided to an ammonia solution and in turn the ammonia and catalyst solution is provided to the absorber tank for mixing with the flue gas. The ammonia and catalyst solution is then oxidized after mixing with the flue gas and the metal chelate catalyst is separated from the spent solution after the  
10 solution has been oxidized.

**SO<sub>2</sub>/NO<sub>x</sub>/Hg REMOVAL FROM FLUE GAS BY AMMONIA  
WET SCRUBBING USING IRON CHELATE CATALYSTS**

**BACKGROUND OF THE INVENTION**

1. **Field of the Invention**

The present invention relates in general to the decontamination of flue gas and in particular to a new and  
5 useful method and system for removing various decontaminants from flue gas through the use of ammonia and iron chelate catalyst scrubbing.

2. **Description of the Related Art**

In the power plant field, it is common to use ammonia in  
10 order to scrub or clean the contaminants from flue gas. Some of the contaminants contained in flue gas comprise NO<sub>x</sub>, SO<sub>2</sub>, Hg, etc. Past laboratory studies have indicated that iron chelates such as Fe<sup>2+</sup> EDTA (Ethylenediaminetetraacetate) catalysts can assist in ammonia scrubbing of flue gas for  
15 removing NO<sub>x</sub>. In turn, several systems and methods were developed using iron chelates as catalysts for assisting in NO<sub>x</sub> removal.

U.S. Patent 4,079,118 discloses a method for removing nitrogen oxides using Ferric ion EDTA complex solutions. This

reference focuses on using Ferric ion for ammonia scrubbing for the removal of  $\text{NO}_x$  only.

U.S. Patent 4,167,578 teaches a method of calcium  
5 scrubbing using an iron EDTA chelate for removing  $\text{NO}_x$  only. The process disclosed, however, utilizes a complex hydrolysis of  $\text{Ca}(\text{NH}_2\text{SO}_3)_2$  in which ammonium sulfate is produced. This ammonia recovery through stripping can be rather expensive.

U.S. Patents 4,288,421 and 4,255,401 teach a scrubbing  
10 process using potassium sulfite and iron chelate salt for  $\text{NO}_x$  and  $\text{SO}_2$  scrubbing involving a complex recovery process which produces sulfur, potassium carbonate and ammonia. U.S. Patent 5,106,601 provides for a  $\text{NO}_x$  and  $\text{SO}_2$  removal process using phosphates emulsion, preferably in a wet scrubber, without a  
15 chelating agent. The by products of this process are calcium and ammonia phosphate.

Presently, there are no known processes or systems for  
efficiently removing  $\text{SO}_x$ ,  $\text{NO}_x$  and Hg from the flue gas in an ammonia wet scrubber through the use of an iron chelate  
20 catalyst.

### SUMMARY OF THE INVENTION

The present invention pertains to method of removing contaminants, such as  $\text{NO}_x$ ,  $\text{SO}_x$ , Hg from a flue gas. The

present invention comprises providing the flue gas to an absorber tank or scrubber reactor. A metal chelate catalyst, such as iron ethylenediaminetetraacetate,  $\text{Fe}^{2+}$  EDTA, is provided to an ammonia solution, which is in turn provided to the absorber tank for mixing with the flue gas. After mixing the ammonia and catalyst solution with the flue gas, the solution is oxidized and the metal chelate catalyst is separated from the solution.

The present invention also pertains to a system for removing contaminants such as  $\text{SO}_x$ ,  $\text{NO}_x$  and Hg from a flue gas which comprises an absorber tank having a flue gas inlet for receiving the contaminated flue gas and a flue gas outlet for passing a clean flue gas from the tank. The absorber tank also has an exit for passing oxidized solution from the absorber tank. A recycler is used to separate the metal chelate catalyst from the used solution back into the system.

The various features of novelty which characterize the invention are pointed out with particularity in the claims annexed to and forming a part of this disclosure. For a better understanding of the invention, its operating advantages and specific objects attained by its uses, reference is made to the accompanying drawings and descriptive matter in which a preferred embodiment of the invention is illustrated.

**BRIEF DESCRIPTION OF THE DRAWINGS**

In the drawings:

Fig. 1 is a schematic view illustrating a system according  
5 to the present invention.

**DESCRIPTION OF THE PREFERRED EMBODIMENTS**

The present invention, as illustrated in Fig. 1, comprises a method and system for removing  $\text{SO}_x$ ,  $\text{NO}_x$  and Hg from a flue gas by ammonia wet scrubbing using an iron chelate catalyst. The system comprises an absorber or scrubber 10  
10 having a flue gas inlet 1 which provides flue gas containing  $\text{SO}_x$ ,  $\text{NO}_x$  and Hg to the absorber 10. The absorber 10 has a plurality of trays 15 located within the absorber 10. An ammonia and catalyst solution 20 is provided to the absorber  
15 10 near the trays 15 through an inlet 22 located near each tray 15. A metal chelate catalyst, such as iron EDTA 21 is provided along with an ammonia solution 4 which makes up the ammonia brine solution 20 which contains both ammonia solution and the iron EDTA catalyst. The ammonia brine solution 20 is  
20 regulated at the absorber 10 by both the inlets 22 and outlets 24 which are also located near the trays 15. <sup>Most</sup> ammonia brine solution 20 is permitted to flow through outlets 24 back to their original source.

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The trays 15 are spaced at least four feet apart from each other in order to minimize entrainment and optimize mass transfer effectiveness within the absorber 10. The present invention does not require any spray nozzles and thus the  
5 trays 15 are sufficient for providing absorption of the flue gas by the ammonia brine solution 20. Ammonia 4 and water 2 are also provided to absorber 10 for maintaining sufficient ammonia concentration control at the different stages 15 for obtaining the required  $\text{SO}_2/\text{NH}_3$  vapor efficiency which is  
10 dependant upon the liquid concentration of bisulfite/sulfite and ammonia 4.

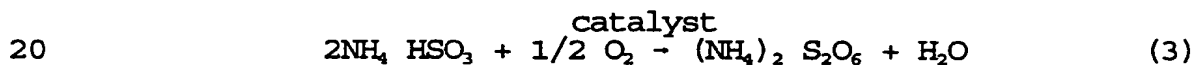
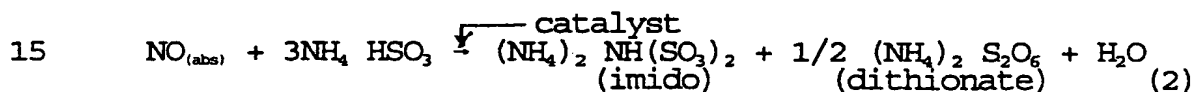
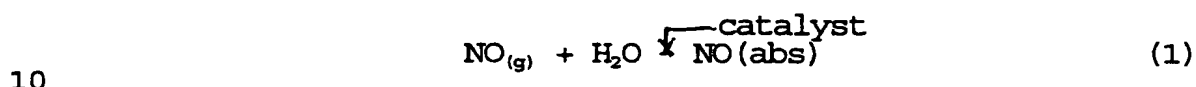
Once the flue gas is mixed at each tray 15 with the ammonia brine catalyst solution 20 for cleaning the flue gas, the solution 20 collects at the bottom of the absorber 10 in  
15 an oxidation zone 18. At this point, the solution 20 in oxidation zone 18 contains absorbed contaminants such as  $\text{NO}_x$ ,  $\text{SO}_x$  and Hg and is exposed to oxidation air 8 for oxidizing the absorbed solution.

The catalyst concentration 21 ranges from 0.05 to 0.30  
20 moles/liter ( $\text{Fe}^{++}$  EDTA) in the liquor 20 depending upon the gas phase  $\text{SO}_2$  and  $\text{NO}_x$  concentration range ( $\text{SO}_2$  500-3000 ppm,  $\text{NO}_x$ , 100 - 600 ppm typical range). The oxidation step is easily accomplished at the bottom of the tower 10 and is controlled for the optimum operation. The basic chemistry will not

change significantly.

Nitric oxide (NO), normally insoluble in water, is absorbed in a bisulfite solution at a moderately low pH, where the NO is catalytically reduced by bisulfite to ammonium ions.

- 5 Bisulfite is oxidized in this reaction to dithionate ion and imido compound as shown by equations (1) and (2) listed below.



- 25 Mercury (Hg) is also absorbed in the solution in the presence of chelate catalyst.

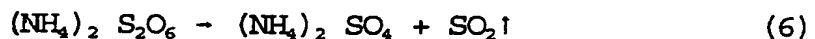
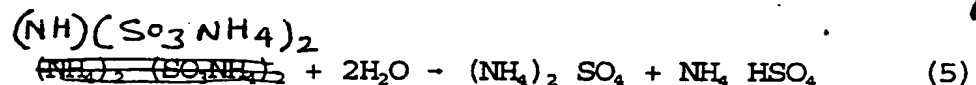
- 30 These side reactions in equations (3) and (4) reduce the availability of bisulfite for the desired reaction. In the presence of the catalyst 21, dithionate formation is predominant over the sulfate formation. Ammonia 4 is supplied to the absorbent solution 20 in order to maintain pH values between 5.5 to 6.5 in the absorber 10. The clean flue gas leaves the absorber at outlet 3 and may be acid washed and reheated to reduce plume formation.



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The spent ammonia brine solution 20 collected at the oxidation zone 18 exits the absorber 10 at outlet 32 located near the oxidation zone 18 at the bottom of absorber 10 for providing the spent brine solution to a catalyst recovery system 30. The spent brine solution from the absorber bottom is oxidized and concentrated prior to it being sent to the catalyst recovery section 30. A catalyst recoverer 34, ~~such~~ <sup>as a centrifuge</sup>, receives the spent brine solution 20, which has been oxidized, and subjects the spent solution to acidifying <sup>by H<sub>2</sub>SO<sub>4</sub>, 35</sup> and cooling in order to crystallize the chelating agent 21 prior to separation by the centrifuge 34. The separated solution is <sup>heated</sup> ~~tested~~ to <sup>120°C</sup> ~~100°C~~ in autoclave where dithionate and imidosulfonate are hydrolysed to decompose into sulfate and bisulfate at a decomposer 36 as shown by equations (5) and (6) below.



Liberated SO<sub>2</sub>, represented at 40, is separated at decomposer 36 and is recycled to absorber tower 10. The acidic solution is then neutralized by ammonia in a neutralizer 38 so as to convert ammonium bisulfate to ammonium sulfate. Hydroxide 42 is separate from the solution and is recycled to the absorber 10 along with catalyst 21 as recovered.

Ammonium sulfate in solution is evaporated by steam heating and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> is crystallized out and filtered by an ammonium sulfate recoverer 39 such as a filter.

Clear scrubbing solution is used for both SO<sub>2</sub> and NO<sub>x</sub>

removal in the tray tower system 10. The number of stages or trays 15 can be reduced by using proprietary type trays. Air toxic metals such as mercury (Hg), are also removed effectively. Total liquid to gas ratio (L/G) will not exceed  
5 40-45 for 95% SO<sub>2</sub> removal and 80-90% NO<sub>x</sub> removal depending upon the inlet concentrations. The byproduct brine can be disposed of as fertilizer.

Ammonia fumes can be reduced to comply with opacity by acid washing of the mist eliminator, or reheating before the  
10 stack emission. Also, a proven wet electrostatic precipitator can be used to reduce fine particulates from the scrubber system. The nitric oxide (NO) is converted to ammonia 4 by the chelating agent 21 and this reduces make-up reagent ammonia. The absorption efficiency for NO<sub>x</sub> increases with  
15 lower oxygen concentration and increases with higher SO<sub>2</sub> concentration. SO<sub>2</sub> and HCl gases are also reduced substantially by ammonia scrubbing at the <sup>Gas</sup>inlet sections ~~22~~. *Ref 13 8/61*

In a normal dry selective catalytic reducer SCR, the limitation for higher SO<sub>2</sub>/SO<sub>2</sub> due to bisulfate formation and  
20 periodic replacement of catalyst is required. Some trace metals are likely to be poisoned and plug up the pores. SO<sub>x</sub>/NO<sub>x</sub>/mercury removal (air toxic) using the present invention with minimum field modification is also possible. Also, particulate removal efficiency is high due to more numbers of  
25 stages and minimum % solids (<1%) in slurry in scrubbing solution.

While a specific embodiment of the invention has been shown and described in detail to illustrate the application of the principles of the invention, it will be understood that  
30 the invention may be embodied otherwise without departing from such principles.

CLAIMSWHAT IS CLAIMED IS:

- 5           1. A method of removing contaminants from a flue gas,  
the method comprising the steps of:  
            providing the flue gas to an absorber tank;  
            providing an ammonia solution to the absorber tank;  
            providing a metal chelate catalyst to the absorber  
10 tank for mixing with the ammonia solution and the flue gas;  
            oxidizing the ammonia and catalyst solution after  
mixing with the flue gas; and  
            separating the metal chelate catalyst from the  
solution after the solution has been oxidized.
- 15           2. The method according to claim 1, wherein the metal  
chelate catalyst comprises iron ethylenediaminetetraacetate,  
Fe<sup>2+</sup> EDTA.
3. The method according to claim 1, including the step  
of recycling the separated metal chelate catalyst.
- 20           4. The method according to claim 3, including the step  
of decomposing a remainder of the solution into sulfates and  
bisulfates after the metal chelate catalyst has been  
separated.
5. The method according to claim 4, wherein the  
25 decomposition is performed by hydrolysing dithionate and  
imidosulfonate.
6. The method according to claim 5, including recycling  
SO<sub>2</sub> decomposed from the remaining solution back into the  
absorber tank.
- 30           7. The method according to claim 6, including the step  
of converting ammonium bisulfate into ammonium sulfate.

8. The method according to claim 7, including the step of filtering out the ammonium sulfate.

9. A system for removing contaminants from a flue gas, the system comprising:

5           an absorber tank having a flue gas inlet for receiving contaminated flue gas and a flue gas outlet for passing a cleaned flue gas from the tank and an exit;  
          means for providing an ammonia and metal chelate catalyst solution to the absorber tank for cleaning the flue  
10 gas;

          oxidation air means for providing oxidation air to the ammonia and metal chelate catalyst solution for oxidizing the solution in the absorber tank, the oxidized solution being passed from the absorber tank through the exit;

15           means for separating the metal chelate catalyst from the oxidized solution; and

          recycling means for recycling the separated metal chelate catalyst back into the system.

20           10. The system according to claim 9, wherein the means for separating the metal chelate catalyst comprises a  
centrifuge after acidifying and cooling. PJB  
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25           11. The system according to claim 10, including a decomposer communicating with the separation means for decomposing a remainder of the oxidized solution into sulfates and bisulfates after the metal chelate is separated.

          12. The system according to claim 11, including a neutralizer communicating with the decomposer for converting bisulfates into sulfates.

30           13. The system according to claim 12, including a filter communicating with the decomposer for filtering out the sulfates.

14. The system according to claim 9, including at least one tray in the absorber tank.

5 15. The system according to claim 14, wherein the means for providing an ammonia and metal chelate catalyst solution comprises an inlet near the tray for providing the solution to the tray and an outlet near the tray for passing an excess of solution from the absorber tank.

10 16. The system according to claim 9, wherein the metal chelate catalyst comprises iron ethylenediaminetetraacetate,  $\text{Fe}^{2+}$  EDTA.

Fig. 1

